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### (54) Hydrosilation method using unsaturated accelerators

(57) A hydrosilation process is disclosed where a silicon hydride is reacted with an unsaturated reactant in the presence of a platinum catalyst and an accelerator selected from 1,7-octadiyne, 1,5-hexadiyne, cyclooctadiene, 5-vinyl-2-norbornene, 4-vinyl-1-cyclohexene, 2,5-bis(t-butylperoxy)-2,5-dimethylhexane, furan, 4H-pyran-4-one, cis-4,7-dihydro-1,3-dioxepin, maleic anhydride and dimethylidiallylmalonate. The accelerators are especially useful for facilitating the hydrosilation of unsaturated reactants where the unsaturation is in the internal portion of the reactant's structure, for example, as in cyclopentene and cyclohexene.

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## Description

This invention provides a hydrosilation process where a silicon hydride is reacted with an unsaturated reactant in the presence of a platinum catalyst and an accelerator selected from 1,7-octadiyne, 1,5-hexadiyne, cyclooctadiene, 5-vinyl-2-norbornene, 4-vinyl-1-cyclohexene, 2,5-bis(t-butylperoxy)-2,5-dimethylhexane, furan, 4H-pyran-4-one, cis-4,7-dihydro-1,3-dioxepin, maleic anhydride and dimethyldiallylmalonate. The accelerators are especially useful for the hydrosilation of unsaturated reactants where the unsaturation is in the internal portion of the reactant's structure.

It is known in the art to produce organosilicon compounds by reacting a silicon hydride containing compound with an unsaturated organic compound in the presence of a catalyst. This reaction is commonly referred to as hydrosilation or hydrosilylation. Typically, the catalyst is platinum metal on a support, a platinum compound in a solvent or a platinum complex.

A major problem known in the art with platinum hydrosilation reactions is catalyst de-activation prior to reaction completion. One method for reactivation of the catalyst is to expose the reaction mixture to oxygen. For example, U.S. Patent 4,578,497, teaches the use of an oxygenated platinum containing catalyst for use in hydrosilating alkylsilanes. U.S. 5,359,111, discloses a method for controlling hydrosilation reaction mixtures by controlling the solution concentration of oxygen in the reaction mixture, relative to the platinum present.

In addition to the problem of de-activation of the platinum catalyst, hydrosilation processes taught in the art are not particularly effective in hydrosilating internal unsaturated bonds in organic molecules. We have discovered that 1,7-octadiyne, 1,5-hexadiyne, cyclooctadiene, 5-vinyl-2-norbornene, 4-vinyl-1-cyclohexene, 2,5-bis(t-butylperoxy)-2,5-dimethylhexane, furan, 4H-pyran-4-one, cis-4,7-dihydro-1,3-dioxepin, maleic anhydride and dimethyldiallylmalonate, act as accelerators for platinum catalyzed hydrosilation processes. These accelerators improve process yield in the presence or absence of oxygen and are particularly effective for enhancing platinum catalyzed hydrosilation of internal unsaturated bonds of organic molecules. A hydrosilation process has now been discovered by us where a silicon hydride is reacted with an unsaturated reactant in the presence of a platinum catalyst and an accelerator selected from 1,7-octadiyne, 1,5-hexadiyne, cyclooctadiene, 5-vinyl-2-norbornene, 4-vinyl-1-cyclohexene, 2,5-bis(t-butylperoxy)-2,5-dimethylhexane, furan, 4H-pyran-4-one, cis-4,7-dihydro-1,3-dioxepin, maleic anhydride and dimethyldiallylmalonate. These accelerators are especially useful for the hydrosilation of unsaturated reactants where the unsaturation is in the internal portion of the compound's structure, for example, as in cyclopentene and cyclohexene. The accelerators are effective in the absence of oxygen activation of the platinum catalyst and are synergistic with oxygen activation of platinum catalyst.

Our hydrosilation process comprises contacting

(A) a silicon hydride described by formula  $R^1_a H_b SiX_{4-a-b}$  where each  $R^1$  is independently selected from alkyls comprising one to 20 carbon atoms, cycloalkyls comprising four to 12 carbon atoms and aryls; each X is an independently selected halogen atom;  $a = 0$  to 3;  $b = 1$  to 3 and  $a + b = 1$  to 4; and

(B) an unsaturated reactant selected from

- (i) substituted or unsubstituted unsaturated organic compounds,
- (ii) silicon compounds comprising substituted or unsubstituted unsaturated organic substituents, and
- (iii) mixtures of (i) and (ii);

in the presence of a platinum catalyst selected from platinum compounds and complexes and an accelerator selected from 1,7-octadiyne, 1,5-hexadiyne, cyclooctadiene, 5-vinyl-2-norbornene, 4-vinyl-1-cyclohexene, 2,5-bis(t-butylperoxy)-2,5-dimethylhexane, furan, 4H-pyran-4-one, cis-4,7-dihydro-1,3-dioxepin, maleic anhydride and dimethyldiallylmalonate.

The contacting of the silicon hydride with the unsaturated reactant is effected in standard type reactors for conducting hydrosilation processes. The contact and reaction is run as a continuous, semi-continuous or batch process.

Silicon hydrides which are useful in our process are described by formula  $R^1_a H_b SiX_{4-a-b}$ , where each  $R^1$  is independently selected from alkyls comprising one to 20 carbon atoms, cycloalkyls comprising four to 12 carbon atoms and aryls;  $a = 0$  to 3,  $b = 1$  to 3 and  $a + b = 1$  to 4.  $R^1$  is a substituted or unsubstituted alkyl, cycloalkyl or aryl as described. It is preferred that each  $R^1$  be independently selected from alkyls comprising one to six carbon atoms. Even more preferred is when each  $R^1$  is methyl.

In the formula describing the silicon halide each X is independently selected halogen atoms and preferably X is a chlorine atom.

Examples of silicon hydrides which are useful in the present process include trimethylsilane, dimethylsilane, triethylsilane, dichlorosilane, trichlorosilane, methylchlorosilane, dimethylchlorosilane, ethylchlorosilane, cyclopentylchlorosilane, methylphenylchlorosilane and (3,3,3-trifluoropropyl)dichlorosilane. A preferred silicon hydride is

selected from methyldichlorosilane and dichlorosilane.

The silicon hydride is contacted with an unsaturated reactant selected from (i) substituted and unsubstituted unsaturated organic compounds, (ii) silicon compounds containing substituted and unsubstituted unsaturated organic substituents and (iii) mixtures of (i) and (ii). "Unsaturated" means a compound contains at least one carbon-carbon double bond.

More specific examples of the unsaturated reactants useful in the process include unsubstituted cycloalkene compounds comprising at least 4 carbon atoms, substituted cycloalkene compounds comprising at least 4 carbon atoms, linear alkene compounds comprising 2 to 30 carbon atoms, branched alkene compounds comprising 4 to 30 carbon atoms and mixtures thereof.

The substituted and unsubstituted cycloalkene compounds useful in our process are those containing one or more unsaturated carbon-carbon bonds in the ring. The unsubstituted cycloalkene compounds are, for example, cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclopentadiene, 1,3-cyclohexadiene and 1,3,5-cycloheptatriene. Substituted unsaturated compounds useful in the present invention are, for example, 3-methylcyclopentene, 3-chlorocyclobutene, 4-phenylcyclohexene and 3-methylcyclopentadiene. The preferred cycloalkene compounds are cyclohexene and cyclopentene, with cyclohexene the most preferred.

Other unsaturated organic compounds useful in the process are linear and branched alkene compounds including compounds with terminal unsaturation such as 1-hexene and 1,5-hexadiene, compounds with internal unsaturation such as trans-2-hexene and unsaturated aryl containing compounds such as styrene and alpha-methylstyrene.

The unsaturated reactants may also contain halogen atoms, oxygen in the form of acids, anhydrides, alcohols, esters, ethers and nitrogen. Two or more of the above described unsaturated organic compounds are used in the present process.

The unsaturated organic compounds containing halogen atoms include vinyl chloride, allyl chloride, allyl bromide, allyl iodide, allyl bromide, methallyl chloride, trichloroethylene, tetrachloroethylene, tetrafluoroethylene, chloroprene, vinylidene chloride and dichlorostyrene.

Suitable unsaturated organic compounds comprising oxygen atoms include ethers such as allyl and vinyl ethers; alcohols such as allyl alcohol (vinyl carbinol), methylvinylcarbinol and ethynylidimethyl-carbinol; acids such as acrylic, methacrylic, vinylacetic, oleic, sorbic, linolenic and esters such as vinyl acetate, allyl acetate, butenyl acetate, allyl stearate, methylacrylate, ethylcrotonate, diallyl succinate and diallyl phthalate. Suitable nitrogen containing unsaturated organic compounds include; indigo, indole, acrylonitrile and allyl cyanide.

Specifically included within the definition of unsaturated organic compounds are those substituted by organofunctional moieties such as:  $\text{CH}_2=\text{CHCH}_2\text{OC(O)C(CH}_3\text{)=CH}_2$ ,  $\text{CH}_2=\text{CHCH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ ,  $\text{CH}_2=\text{CHCH}_2\text{NH}_2$ ,  $\text{CH}_2=\text{CHCH}_2\text{SH}$ ,  $\text{CH}_2=\text{CHSi}[\text{O}(\text{CH}_2)_2\text{OCH}_3]_3$ .



40  $\text{CH}_2=\text{CHCH}_2\text{N}(\text{HCl})\text{HCH}_2\text{CH}_2\text{NHCH}_2(\text{C}_6\text{H}_4)\text{CH=CH}_2$  and similar compounds.

The unsaturated organic compound is a silicon compound containing substituted and unsubstituted organic substituents as described by, for example, formulas  $(\text{CH}_2=\text{CH}(\text{CH}_2)_g)_h\text{R}^1\text{Si}(\text{OR}^1)_{4-h-i}$  and  $(\text{CH}_2=\text{CH}(\text{CH}_2)_g)_h\text{R}^1\text{SiCl}_{4-h-i}$ , where  $\text{R}^1$  is as previously described,  $g = 0$  to  $12$ ,  $h = 1$  to  $3$ ,  $i = 0$  to  $3$  and  $h + i = 1$  to  $4$ .

45 Prior to contact of the silicon hydride with the unsaturated reactant, it is preferable to treat or purify the unsaturated reactant. Methods useful for treating or purifying the unsaturated reactants are those known in the art for treating or purifying unsaturated organic compounds and include but are not limited to distillation and treatment with an adsorbent such as activated alumina or molecular sieves.

The relative amounts of silicon hydride and unsaturated reactant used in the present process are varied within wide 50 limits. Although one unsaturated carbon-carbon linkage per silicon bonded hydrogen atom is stoichiometric, there is no requirement that the process be conducted under stoichiometric conditions. Generally, it is preferred that the process is conducted with a stoichiometric excess of silicon hydride. Preferred is when the process is run with 0.1 to 10 percent stoichiometric excess of silicon hydride.

The silicon hydride and unsaturated reactant are contacted in the presence of a catalyst selected from platinum 55 compounds and platinum complexes. Any platinum containing material which effects the reaction between the silicon hydride and an unsaturated carbon-carbon bond of the unsaturated organic compound is useful in our invention. Examples of platinum catalysts useful in our process are described in U.S. Patents 4,578,497, 3,220,972, 2,823,218 and 3,419,593.

Acceptable platinum catalysts are chloroplatinic acid, chloroplatinic acid hexahydrate, Karstedt's catalyst (i.e. a complex of chloroplatinic acid with sym-divinyltetramethylsiloxane), dichlorobis(triphenylphosphine)-platinum(II), cis-dichlorobis(acetonitrile)-platinum(II), dicarbonyldichloroplatinum(II), platinum chloride, platinum oxide and platinum vinylsiloxane complexes such as a neutralized complex of platinum dichloride with sym-divinyltetramethylsiloxane.

5 A preferred platinum catalyst is selected from chloroplatinic acid, chloroplatinic acid hexahydrate and platinum vinylsiloxane complexes such as a neutralized complex of chloroplatinic acid or platinum dichloride with sym-divinyltetramethylsiloxane. An example of a platinum catalyst is described in U.S. Patent 5,175,325.

10 Catalyst concentrations providing one mole equivalent of platinum per billion mole equivalent of unsaturated carbon-carbon bonds added to the process by the unsaturated reactant are useful in our process. Catalyst concentrations providing as high as one mole equivalent of platinum per one thousand mole equivalents of unsaturated carbon-carbon bonds added to the process by the unsaturated reactant are useful also. Higher concentrations of platinum will also work in our invention. A preferred concentration of platinum catalyst is 1 to 1000 mole equivalents of platinum per  $1 \times 10^6$  mole equivalents of unsaturated carbon-carbon bonds provided to the process by the unsaturated reactant.

15 The catalyst is dissolved in a solvent for ease of handling. Suitable solvents are non-polar hydrocarbon solvents such as benzene, toluene and xylene and polar solvents such as alcohols, glycols and esters.

20 The process is carried out in the presence of accelerators selected from 1,7-octadiyne, 1,5-hexadiyne, cyclooctadiene, 5-vinyl-2-norbornene, 4-vinyl-1-cyclohexene, 2,5-bis(t-butylperoxy)-2,5-dimethylhexane, furan, 4H-pyran-4-one, cis-4,7-dihydro-1,3-dioxepin, maleic anhydride and dimethyldiallylmalonate. The above listed accelerators are commercially available.

25 An effective concentration of the selected accelerator is added to the present process, where an effective concentration is one that initiates the reaction between the silicon hydride and the unsaturated organic compound, accelerates the rate of the reaction or reduces loss of reactivity of the catalyst in the process. A useful effective concentration of the accelerator is 0.01 to 20 wt % of the weight of the unsaturated reactant. Preferred is when the accelerator is 0.1 to 10 wt % of the weight of the unsaturated reactant.

30 The presence of oxygen in our process enhances reaction parameters such as the reaction rate and selectivity of addition when the solution concentration of oxygen is controlled relative to platinum catalyst in the reaction mixture. Oxygen is normally added to the reaction mixture by bubbling it into one of the reactants or by bubbling it into the reaction mixture. Feeding the oxygen into the vapor space of the reactor or by purging the reactor system with oxygen is possible also, but often is not as effective due to mass transfer considerations.

35 The effective amount of oxygen added to our process depends on such factors as operating conditions, the reactants and the amount of catalyst present. It is preferred to introduce the oxygen into the process combined with an inert gas at an oxygen level of parts per million to 20 wt %, based on the combined weights of the oxygen and inert gas. More preferred is when the oxygen is diluted in an inert gas to 0.1 to 40 wt %. The inert gas is usually nitrogen or argon. Typically, the preferred amount of oxygen to be added to the process is determined by monitoring the rate of reaction and by-product formation. A suitable procedure for adding oxygen to our hydrosilation method is described in U.S. Patent 5,359,111.

The following examples are provided to illustrate our invention.

#### Example 1

40 A stock mixture was prepared in an argon purged and blanketed bottle. The stock mixture comprised 7% molar excess of methyldichlorosilane in cyclohexene which had been treated with 13X molecular sieves. A catalyst containing 6  $\times 10^{-5}$  moles of platinum, as a complex prepared by the reaction of  $\text{PtCl}_2$  with sym-divinyltetramethylsiloxane, per mole of cyclohexene was added to the stock mixture. A 2 ml aliquot of this catalyzed stock solution was transferred to 45 argon-purged glass tubes and the accelerators listed in Table 1 were added to individual tubes at a concentration of 0.4 vol %. The tubes were cooled, heat sealed under an argon purge and heated at 80°C. for three hours. After three hours, the tubes were cooled and contents analyzed by gas chromatography using a thermal conductivity detector (GC-TC). Results are reported in Table 1 as the Normalized Area % of cyclohexylmethyldi-chlorosilane ( $\text{C}_6\text{H}_{11}\text{MeSiCl}_2$ ) under the GC-TC trace minus the area % of cyclohexene as 100%.

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TABLE 1

Accelerator	$\text{C}_6\text{H}_{11}\text{MeSiCl}_2$ Normalized Area %
None	60.8
Cyclooctadiene	91.2

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TABLE 1 (continued)

Accelerator	C <sub>6</sub> H <sub>11</sub> MeSiCl <sub>2</sub> Normalized Area %
5 MeViSi(MBO) <sub>2</sub>	99.1
None	61.7
10 1,5-Hexadiyne	77.8
Furan	92.0
15 2-Methyl-1-hexen-3-yne	86.4
4H-Pyran-4-one	95.5
None	52.5
15 1,7-Octadiyne	96.5
Dimethyldiallylmalonate	70.1
None	66.3
20 cis-4,7-Dihydro-1,3-dioxepin	79.4
None	41.2
5-Vinyl-2-norbornene	93.7
4-Vinyl-1-cyclohexene	80.8
25 Maleic anhydride	90.4

Example 2

30 A stock mixture was prepared in an argon purged and blanketed bottle. The stock mixture comprised seven molar percent excess of methyldichlorosilane in cyclohexene which had been treated with 13X molecular sieves. A catalyst containing  $6.9 \times 10^{-5}$  moles of a platinum complex which is the neutralized reaction product of chloroplatinic acid and sym-divinyltetramethyldisiloxane, per mole of cyclohexene was added to the stock mixture. A 2 ml aliquot of this catalyzed stock solution was transferred to a argon-purged glass tube and the accelerator 2,5-bis(t-butylperoxy)2,5-dimeth-  
 35 ylhexane was added to the tube at a concentration of 1 volume percent. The tube was cooled, heat sealed under an argon purge and heated at 80°C. for three hours. At the end of three hours the tube was cooled and the contents analyzed by gas chromatography using a thermal conductivity detector (GC-TC). The results of this analysis in Area % are 7.0 cyclohexene, 4.1 methyldichlorosilane and 82.2 cyclohexylmethyldichlorosilane under the GC-TC trace.

40 **Claims**

## 1. A hydrosilation process comprising contacting

45 (A) a silicon hydride described by formula R<sup>1</sup><sub>a</sub>H<sub>b</sub>SiX<sub>4-a-b</sub>, where each R<sup>1</sup> is independently selected from alkyls comprising 1 to 20 carbon atoms, cycloalkyls comprising 1 to 12 carbon atoms and aryls; each X is an inde-  
 p-  
 pendently selected halogen atom; a = 0 to 3, b = 1 to 3 and a + b = 1 to 4 ; and  
 (B) an unsaturated reactant selected from

50 (i) substituted and unsubstituted unsaturated organic compounds,  
 (ii) silicon compounds containing substituted or unsubstituted unsaturated organic substituents, and  
 (iii) mixtures of (i) and (ii);

55 in the presence of a platinum catalyst selected from platinum compounds and complexes and an accelerator selected from 1,7-octadiyne, 1,5-hexadiyne, 5-vinyl-2-norbornene, 2,5-bis(t-butylperoxy)-2,5-dimethylhexane, furan, 4H-pyran-4-one, maleic anhydride, cis-4,7-dihydro-1,3-dioxepin and dimethyldiallylmalonate.

2. A process according to claim 1, where the silicon hydride is selected from trimethylsilane, dimethylsilane, triethyl-  
 silane, dichlorosilane, trichlorosilane, methyldichlorosilane, dimethylchlorosilane, ethyldichlorosilane, cyclopentyl-

dichlorosilane, methylphenylchlorosilane and (3,3,3-trifluoropropyl)-dichlorosilane.

3. A process according to claim 1, where the unsaturated reactant is selected from unsubstituted cycloalkene compounds comprising at least 4 carbon atoms, substituted cycloalkene compounds comprising at least 4 carbon atoms, linear alkene compounds comprising 2 to 30 carbon atoms, branched alkene compounds comprising 4 to 30 carbon atoms and mixtures thereof.
4. A process according to claim 1, where the platinum catalyst is selected from chloroplatinic acid, chloroplatinic acid hexahydrate and platinum vinylsiloxane complexes.
- 10 5. A process according to claim 1, where the concentration of the accelerator is 0.01 to 20 wt % of the weight of the unsaturated reactant.

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## EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 731 104 A (WACKER CHEMIE GMBH) 11 September 1996 * page 3, column 3 * -----	1-5	C07F7/14  <b>TECHNICAL FIELDS SEARCHED (Int.Cl.6)</b> C07F
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>6 May 1999</b>	Examiner <b>Bader, K</b>
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